

GRANT AREA

SIMULATION STUDIES FOR SURFACES
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SIMULATION STUDIES FOR SURFACES AND MATERIALS STRENGTH

In accordance with the original proposal, during this period the following investigations were carried out.

(1) *An analysis of the structure-energy relationship in small clusters.* This study is very closely related to the improvement of the potential energy functions which are suitable and simple enough to be used in atomistic simulation studies. Parameters obtained from ab initio calculations for dimers and trimers of *Al* were used to estimate energetics and global minimum energy structures of clusters containing up to 15 *Al* atoms. (2) *Modeling of the collision process for atoms impinging on surfaces.* In this simulation study we analyzed qualitative aspects of the *O* atom collision with the graphite surface. Four different *O*/graphite systems were considered and the aftermath of the impact was analyzed. (3) *Simulation of thin amorphous Si films on crystalline Si substrates.* Parameters obtained in an earlier study were used to model an exposed amorphous *Si* surface and an *a-Si/c-Si* interface. Structural details for various film thicknesses were investigated at an atomistic level.

1. Structure-Energy Relationship in Small Clusters

To calculate low energy configurations of small *Al* clusters we employed a semiempirical potential energy function comprising two- and three-body interactions which were approximated by the Lennard-Jones and Axilrod-Teller potentials, respectively. Parameters for these functions were evaluated from fits to Al_2 and Al_3 energies obtained from ab initio all electron calculations. The fitting procedure was carried out to produce the best result around the minimum regions of the potential energy. Assuming reduced parameters for the *Al* system, the value of the dimensionless three-body parameter was found to be in the interval of $Z^* = 0.4 - 0.5$.

For the smaller clusters (up to $n = 6$, where n represents the total number of atoms in the cluster), the ab initio results were best reproduced with a value of Z^* around 0.5. For larger clusters ($n > 6$) it was found that the value of Z^* should be somewhat reduced. However, this conclusion, at this stage, is rather qualitative because the comparison was made based solely on the ab initio result of Al_{13} which was calculated at a less approximate level than the small cluster cases. In order to analyze the general trends in the structure-energy relationship for relatively larger Al clusters, calculations were carried out considering $Z^* = 0.425$, as a prototype example. In this investigation we calculated global minimum energy configurations for clusters containing 7 – 15 Al atoms.

Minimizations were performed in two basic steps. First, a Monte-Carlo technique was employed in connection with a damping method to search the configurational space and find the catchment area belonging to the lowest minimum. The Monte-Carlo runs were started from a randomly chosen initial configuration confined in a volume to give the correct density of the Al crystal. We performed, for each case, approximately 10^5 individual Monte-Carlo steps during which the total energy of the system was monitored continuously and the configuration corresponding to the lowest energy was saved. In the second part, this lowest energy configuration was used as an input in a fast minimization routine to further minimize the energy and obtain the energetically most favorable structure of the run. For each cluster, the whole minimization procedure was repeated at least 50 times (with different initial configurations) and the global minimum was chosen as the one with the lowest-lying energy level among all.

The most important conclusions drawn from this study were: (i) The lowest energy structures do not always have high symmetry. (ii) Two-dimensional, as well as three-dimensional, structures may be the low-lying state. (iii) The potential energy function employed in this study is flexible enough to produce results consistent with ab initio calculations.

2. Modeling of the collision process for atoms impinging on surfaces

Simulation calculations for the collision process of a free O atom onto graphite surfaces were carried out using a molecular dynamics technique based on the Nordsieck-Gear algorithm. In the calculation of energies and forces among the particles we employed the Lennard-Jones and the Axilrod-Teller potentials to represent two- and three-body interactions, respectively. The potential energy parameters for carbon were taken from an earlier study based on the same potential energy function. Some shortcomings of these parameters (as discussed in previous reports) do still exist. Parameters considered for C were: $\epsilon_{(C-C)} = 5.437 \text{ eV}$, $r_{(C-C)}^0 = 1.439 \text{ \AA}$ and $Z_{CCC} = 129.53 \text{ eV.\AA}^9$. These parameters are able to reproduce acceptable cohesive energy and the first volume derivative values for graphite, but fail to produce correct stress tensor values in all three directions. For cross interaction parameters we considered: $\epsilon_{(C-O)} = 5.0 \text{ eV}$, $r_{(C-O)}^0 = 1.250 \text{ \AA}$ and $Z_{CCO} = 130.0 \text{ eV.\AA}^9$. In all cases the impact velocity of O was chosen to be approximately 5 eV , with an initial surface temperature of $1^\circ K$. Because of the high kinetic energy assigned for the O atom the time step was taken to be 10^{-16} sec. throughout the molecular dynamics runs. Calculations were performed for four different systems. In the first two of these cases, an ideal “defect free” graphite surface was assumed, while for the other two cases we considered a surface with a ledge. (i) First, the impinging O atom was chosen to collide into a hole site. In this case, O diffused through the hexagonal C -ring into the first interlayer spacing (between the first and second layers) and localized as an intercalated O atom. The surface damage was found to be minimal. (ii) Second, the O atom was assigned to hit near the center between two neighboring carbon atoms located on the exposed surface. This collision created considerable surface damage and, as in the previous case, O was found to be trapped between the first and second layers. (iii) In the third case, the O atom, on a perpendicular trajectory to the surface plane, collided head-on with a surface carbon atom near the ledge. As in the second case, the impact region was damaged. In this case, however, the O atom bounced back from the surface

and was leaving the system (as observed during the time frame of the simulation). (iv) In the last case, the O atom hit a ledge carbon atom with an incident angle of 45 degrees. As in the previous cases, the O atom was found to be trapped in the first interlayer spacing and considerable damage and disorder around the ledge were observed. In the last three cases, surface damage caused by the impact of the O atom was quite extensive, the local order of the hexagonal arrays in the top layer was lost and, probably, some degree of amorphization took place around the impact region. During this investigation we were unable to detect any desorbing C atoms leaving the system as a result of the impact. This is clearly due to the strong bonding which exists among C atoms at the surface layer of the graphite lattice. However, once the top surface layer is damaged and its ordered structure no longer exists, the result of subsequent impact by O atoms may be quite different.

3. Simulation of Thin Amorphous Si Films

The thin layer of amorphous silicon ($a - Si$) on the crystalline silicon ($c - Si$) substrate was created by melting and then quenching the surface region of a properly oriented silicon crystal. Simulation calculations were performed using a molecular dynamics technique. The code uses the Lennard-Jones and the Axilrod-Teller potentials to approximate the two- and three-body interactions. Melting was achieved by raising the temperature of a thin region at the free surface to a value above $1920^\circ K$ which was found earlier to be the melting point of Si using the same potential energy function. All the Si atoms in the surface region were allowed to move under the molecular dynamics code, while in the crystalline region below, the atoms were constrained to stay at their lattice points. Two-dimensional periodic boundary conditions were applied in the directions parallel to the exposed surface and all possible interactions between moving and fixed atoms were included for calculating forces and energies. Three thousand molecular dynamics steps at $T = 1950^\circ K$ were found to be sufficient for melting. Quenching was achieved by lowering the system temperature in a single step with temperature rescaling

(at $T = 1.0^\circ K$) applied for approximately 500 steps to drain the excess kinetic energy from the system. The system was then permitted to equilibrate freely and it eventually stabilized at $T = 450^\circ K$.

In this study, both $Si(100)$ and $Si(111)$ substrates were used. For the $Si(100)$ case, three different film thicknesses were considered in order to investigate the film thickness effect on the structural features. For the $Si(111)$ case, a large film thickness was considered to investigate the substrate orientation effect on the structural features. The most striking feature was found to be the presence of a "skin" or inordinately dense layer of atoms at the free surface of the amorphous region underlaid by a much less dense zone with large holes or cavities. This feature is present for all layer thicknesses studied. One can be reasonably assured that it is an equilibrium phenomenon and not a film thickness artifact. This high density surface skin is reminiscent of the strongly compressive stress tensor found at the $Si(111)$ free surface. A second striking feature is the $a - Si/c - Si$ interface void region for the $Si(111)$ substrate compared to the $Si(100)$ substrate. This occurs because of the high atomic density and the triangular network of the (111) surface. Silicon atoms from the amorphous region cannot approach the crystalline surface as closely as they can for the (100) case with a square atomic network. Of course, this may be partially due to the fact that the crystalline substrate was held rigid.